

**ENVIRONMENTALLY COMPATIBLE
HYDROCARBON BLEND DRILLING FLUID**

BACKGROUND OF THE INVENTION

In rotary drilling there are a variety of functions and characteristics that are expected of a drilling fluid ("drilling mud" or simply "mud"). The drilling fluid is expected to carry cuttings from beneath the bit, transport them up the annulus, and permit their separation at the surface while at the same time the rotary bit is cooled and cleaned. A drilling mud is also intended to reduce friction between the drill string and the sides of the hole while maintaining the stability of uncased sections of the borehole. Likewise the drilling fluid is formulated to prevent unwanted influxes of formation fluids from permeable rocks penetrated and likewise to form a thin, low permeability filter cake, which seals pores and other openings and formations, penetrated by the bit. Finally, the drilling fluid is used to collect and interpret information available from drill cuttings, cores and electrical logs.

Drilling fluids are typically classified by the U.S. Environmental Protection Agency ("EPA") in the following manner:

"Drilling Fluid" means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

(a) "Water-Based Drilling Fluid" means the continuous phase and suspending medium for solids is a water-miscible fluid, regardless of the presence of oil.

(b) "Non-Aqueous Drilling Fluid" means the continuous phase and suspending medium for solids is a water-immiscible fluid, such as oleaginous materials (e.g., mineral oil, enhanced mineral oil, paraffinic oil, C₁₆-C₁₈ internal olefins, and C₈-C₁₆ fatty acid/2-ethylhexyl esters).

(i) "Oil-Based" means the continuous phase of the drilling fluid consists of diesel oil, mineral oil, or some other oil, but contains no synthetic material or enhanced mineral oil.

(ii) "Enhanced Mineral Oil-Based" means the continuous phase of the drilling fluid is enhanced mineral oil.

1 (iii) "Synthetic-Based" means the continuous phase of the drilling fluid is a
2 synthetic material or a combination of synthetic materials.

3 The EPA further defines Diesel oil, Enhanced Mineral Oil and Synthetic Material
4 in the following manner:

5 "Diesel Oil" refers to the grade of distillate fuel oil, as specified in the American
6 Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975-91,
7 that is typically used as the continuous phase in conventional oil-based drilling fluids.
8 This incorporation by reference was approved by the Director of the Federal Register in
9 accordance with 5 U.S.C. 552(a) and 1 CFR Part 51. Copies may be obtained from the
10 American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
11 Copies may be inspected at the Office of the Federal Register, 800 North Capitol Street,
12 NW., Suite 700, Washington, DC. A copy may also be inspected at EPA's Water Docket,
13 401 M Street SW., Washington, DC 20460.

14 "Enhanced Mineral" oil as applied to enhanced mineral oil-based drilling fluid
15 means a petroleum distillate which has been highly purified and is distinguished from
16 diesel oil and conventional mineral oil in having a lower polycyclic aromatic
17 hydrocarbon (PAH) content. Typically, conventional mineral oils have a PAH content on
18 the order of 0.35 weight percent expressed as phenanthrene, whereas enhanced mineral
19 oils typically have a PAH content of 0.001 or lower weight percent PAH expressed as
20 phenanthrene.

21 "Synthetic Material" as applied to synthetic-based drilling fluid means material
22 produced by the reaction of specific purified chemical feedstock, as opposed to the
23 traditional base fluids such as diesel and mineral oil which are derived from crude oil
24 solely through physical separation processes. Physical separation processes include
25 fractionation and distillation and/or minor chemical reactions such as cracking and hydro
26 processing. Since they are synthesized by the reaction of purified compounds, synthetic
27 materials suitable for use in drilling fluids are typically free of polycyclic aromatic
28 hydrocarbons (PAH's) but are sometimes found to contain levels of PAH up to 0.001
29 weight percent PAH expressed as phenanthrene. Internal olefins and vegetable esters are
30 two examples of synthetic materials suitable for use by the oil and gas extraction industry
31 in formulating drilling fluids. Internal olefins are synthesized from the isomerization of

1 purified straight-chain (linear) hydrocarbons such as C₁₆-C₁₈ linear alpha olefins. C₁₆-C₁₈
2 linear alpha olefins are unsaturated hydrocarbons with the carbon to carbon double bond
3 in the terminal position. Internal olefins are typically formed from heating linear alpha
4 olefins with a catalyst. The feed material for synthetic linear alpha olefins is typically
5 purified ethylene. Vegetable esters are synthesized from the acid-catalyzed esterification
6 of vegetable fatty acids with various alcohols. EPA listed these two branches of synthetic
7 fluid base materials to provide examples, and EPA does not mean to exclude other
8 synthetic materials that are either in current use or may be used in the future. A synthetic-
9 based drilling fluid may include a combination of synthetic materials.

10 On both offshore and inland drilling barges and rigs, drill cuttings are conveyed
11 up the hole by a drilling fluid. Water based drilling fluids may be suitable for drilling in
12 certain types of formations; however, for proper drilling in other formations, it is
13 desirable to use a non-aqueous drilling fluid. With a non-aqueous drilling fluid, the
14 cuttings, besides ordinarily containing moisture, are necessarily coated with an adherent
15 film or layer of oleaginous drilling fluid, which may penetrate into the interior of the
16 cuttings. This is true despite the use of various vibrating screens, mechanical separation
17 devices and various chemical and washing techniques. Currently, in outer continental
18 shelf waters of the U.S., cuttings drilled using diesel based and mineral oil based non-
19 aqueous drilling fluids are prohibited from discharge and therefore require an alternate
20 method of disposal in order to meet regulatory requirements, most of which are more
21 expensive and more inconvenient than discharge of water based drilling fluids.

22 Regulations are imposed by governmental regulatory agencies concerning
23 discharges of drilling fluids and associated cuttings. These regulations have not only
24 made the use of diesel oil based and mineral oil based non-aqueous drilling fluid more
25 costly but in some places difficult or impossible to use in compliance with the EPA
26 guidelines and permits. Environmental concerns have prompted the development of a
27 new drilling fluid. This drilling fluid is designed to meet the technology-based standards
28 and water quality standards for discharge in compliance with EPA guidelines and
29 Permits.

30 The EPA has specified protocol for meeting technology-based standards
31 associated with discharge of cuttings associated with non-aqueous drilling fluids. These

1 requirements can be found in the Effluent Limitation Guidelines for discharge of
 2 synthetic-based drilling mud and other non-aqueous based drilling fluids and the General
 3 permits that allow authorize discharge of synthetic-based drilling muds and other non-
 4 aqueous based drilling fluids. Detailed accounts of the procedures for measuring toxicity,
 5 biodegradation and PAH content and synthetic materials is described in the guidelines
 6 and in the permits. From the guidelines the following references are used:

7 Sediment toxicity: "Standard Guide for Conducting 10-day Static Sediment
 8 Toxicity Tests with Marine and Estuarine Amphipods," 1992, after preparing the
 9 sediment according to the method specified in Appendix 3 of subpart A of 40 CFR part
 10 435. This incorporation by reference was approved by the Director of the Federal
 11 Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained
 12 from the American Society for Testing and Materials, 100 Barr Harbor Drive, West
 13 Conshohocken, PA, 19428. Copies may be inspected at the Office of the Federal
 14 Register, 800 North Capitol Street, NW., Suite 700, Washington, DC. A copy may also
 15 be inspected at EPA's Water Docket, 401 M Street SW., Washington, DC 20460.

16 Biodegradation: ISO 11734:1995 (specified at § 435.11(e)) method: "Water
 17 quality—Evaluation of the 'ultimate' anaerobic biodegradability of organic compounds
 18 in digested sludge—Method by measurement of the biogas production (1995 edition)" as
 19 modified for the marine environment (Appendix 4 of subpart A of 40 CFR part 435).
 20 This incorporation by reference was approved by the Director of the Federal Register in
 21 accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the
 22 American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY
 23 10036. Copies may be inspected at the Office of the Federal Register, 800 North Capitol
 24 Street, NW., Suite 700, Washington, DC. A copy may also be inspected at EPA's Water
 25 Docket, 401 M Street SW., Washington, DC 20460.

26 PAH: Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as
 27 determined by EPA Method 1654, Revision A, (specified at § 435.11(u)) entitled "PAH
 28 Content of Oil by HPLC/UV," December 1992, which is published in Methods for the
 29 Determination of Diesel, Mineral, and Crude Oils in Offshore Oil and Gas Industry
 30 Discharges, EPA-821-R-92-008. This incorporation by reference was approved by the
 31 Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51.

1 Copies may be obtained from the National Technical Information Service, Springfield,
2 VA 22161, 703-605-6000. Copies may be inspected at the Office of the Federal
3 Register, 800 North Capitol Street, NW., Suite 700, Washington, DC. A copy may also
4 be inspected at EPA's Water Docket, 401 M Street SW., Washington, DC 20460.

5 Also described in the guidelines the procedures for determination or synthetic-
6 based drilling mud drilling fluid toxicity is as follows:

7 4-day LC50 of C16-C18 internal olefin drilling fluid/4-day LC50 of drilling fluid
8 removed from drill cuttings at the solids control equipment as determined by ASTM E
9 1367-92 (specified at § 435.11(ee)) method: "Standard Guide for Conducting 10-day
10 Static Sediment Toxicity Tests with Marine and Estuarine Amphipods," 1992, after
11 preparing the sediment according to the method specified in Appendix 3 of subpart A of
12 this part. This incorporation by reference was approved by the Director of the Federal
13 Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained
14 from the American Society for Testing and Materials, 100 Barr Harbor Drive, West
15 Conshohocken, PA, 19428. Copies may be inspected at the Office of the Federal
16 Register, 800 North Capitol Street, NW., Suite 700, Washington, DC. A copy may also
17 be inspected at EPA's Water Docket, 401 M Street SW., Washington, DC 20460.

18 These same procedures are further described in the EPA Region VI general permit
19 GMG 290,000 as follows: Toxicity: Part I, Section D.8 of GMG 290000; Biodegradation:
20 Part I, Section D.9 of GMG 290000; PAH : Part I, Section D.10 of GMG 290000

21 Several publications describe the use of mineral oils for low toxicity oil-based
22 muds. However, mineral oils that were once considered to be toxicologically and
23 environmentally superior to crude oil or diesel oil based drilling muds are now also
24 prohibited from discharge under increasingly stringent environmental regulations.
25 Several attempts to develop modified environmentally acceptable fluids have been made.
26 In many instances these fluids are not true hydrocarbon fluids and require an aqueous
27 continuous phase that does not provide desirable functional characteristics, for instance,
28 shale stability derived with diesel oil based muds. Thus, there is a long felt need in the oil
29 and gas exploration industry for an environmentally acceptable drilling fluid which either
30 performs as well a diesel oil based drilling fluid has now been achieved by the present
31 invention.

1 SUMMARY OF THE INVENTION

2 The present invention includes a biodegradable wellbore fluid that includes a first
 3 synthetic internal olefin having from 16 to 18 carbon atoms, a second synthetic internal
 4 olefin having between 15 and 18 carbon atoms and a third synthetic internal olefin having
 5 15-16 carbon atoms. As the term is used in this disclosure a C₁₆₋₁₈ IO is defined as
 6 having a C₁₆ isomer content of greater than 50% w/w and a C₁₈ isomer content greater
 7 than 30% w/w. As the term is used in this disclosure a C₁₅₋₁₈ IO is defined as having a
 8 C₁₅ isomer content of greater than 20% w/w; a C₁₆ isomer content greater than 20%; a C₁₇
 9 isomer content greater than 20%; and a C₁₈ isomer content greater than 15% w/w. As the
 10 term is used in this disclosure a C₁₅₋₁₆ IO is defined as having a C₁₅ isomer content of
 11 greater than 40% w/w and a C₁₆ isomer content greater than 40% w/w. As the term is
 12 used in this disclosure a C₁₆ alpha olefin is defined as having a C₁₆ isomer content of
 13 greater than 90% w/w. The fluids may contain a mixture of isomers so long as the
 14 content of the other isomers does not exceed those of the isomers that define the fluid.

15 The components of the illustrative wellbore fluid are blended such that the desired
 16 characteristics of toxicity and biodegradability are balanced to achieve compliance with the
 17 base stock limitation requirements for discharge. One such illustrative embodiment
 18 achieves this result by utilizing a core blend formulation in which the first internal olefin
 19 is present in a range up to 70 percent by volume of the wellbore fluid and wherein the
 20 second internal olefin is present in range of up to 70 percent by volume of the wellbore
 21 fluid and wherein the third olefin is present in range of up to 60 percent by volume of the
 22 wellbore fluid. In addition to the first core blend, variations of the base stock blend
 23 ratios and interpolations between these blends are also included in the present invention.

Blend ratio	C ₁₆ - C ₁₈	C ₁₅ - C ₁₈	C ₁₅ - C ₁₆
Core	50	25	25
1	25	50	25
2	25	25	50
3	30	70	0
4	70	30	0
5	60	0	40
6	40	0	60

1

2 Optionally, the illustrative fluid can include a C₁₆ alpha olefin. In such instances,
3 the core blend and associated variations and interpolations between variations would be
4 as follows

5

Blend ratio variation	C ₁₆ -C ₁₈	C ₁₅ -C ₁₈	C ₁₅ -C ₁₆	C ₁₆
Core	50	20	15	15
1	50	30	10	10
2	50	15	20	15
3	50	10	30	10
4	60	20	10	10
5	40	20	20	20
6	70	30	0	0

6

7 C₁₆ alpha olefin is present at up to 20 percent by volume of the base fluid in the
8 core blend. A person of skill in the art should understand and appreciate that the
9 illustrative well bore fluid may further include a non-oleaginous phase, typically as an
10 internal phase. By doing so a non-aqueous drilling fluid is preferably formed. When
11 included the non-oleaginous phase constitutes from about 1% to about 70% by volume of
12 said fluid. Such a non-oleaginous phase may be selected from fresh water, seawater, a
13 brine containing organic or inorganic dissolved salts, a liquid containing water-miscible
14 organic compounds, and combinations thereof. The fluids of the present invention may
15 further contain additional components depending upon the end use of the non-aqueous
16 drilling fluid so long as they do not adversely impact the toxicity of the fluids described
17 herein to a point which they can no longer meet the toxicity requirements in the
18 Guidelines and the General Permit. For example, alkali reserve, wetting agents,
19 organophillic clays, viscosifiers, weighting agents, bridging agents and fluid loss control
20 agents may be added to the fluid compositions of this invention for additional functional
21 properties. The addition of such agents should be well known to one of skill in the art of
22 formulating drilling fluids and muds. When included the weighting agent is selected

1 from the group including calcium carbonate, dolomite, siderite, barite, celestite, iron
2 oxides, manganese oxides, ulexite, carnalite, sodium chloride and combinations thereof
3 and similar such weighting agents known in the art.

4 Alternatively, the present invention is considered to be a method of formulating
5 the continuous phase of a hydrocarbon based drilling fluid. In one such illustrative
6 embodiment, the method includes: determining the toxicity of a selection of hydrocarbon
7 components; determining the biodegradability of the selection of hydrocarbon
8 components determining the PAH contents of the hydrocarbon components; and blending
9 the selection hydrocarbon components in a manner which produces a hydrocarbon based
10 drilling fluid that consistently passes with a score of ≤ 1 using the "10-day Static
11 Sediment Toxicity Tests with Marine and Estuarine Amphipods," as disclosed in the
12 guidelines and the general permits including GMG290000 and consistently passes with a
13 biodegradation rate ratio ≤ 1 using the modified ISO 11734 test described in the
14 guidelines and the permit. The selection of hydrocarbons in the illustrative embodiment
15 is preferably from the group including a first synthetic internal olefin having from 16 to
16 18 carbon atoms, a second synthetic internal olefin having from 15 to 18 carbon atoms; a
17 third synthetic internal olefin having from 15 to 16 carbon atoms and an alpha olefin
18 having 16 carbon atoms. That is to say, another illustrative embodiment of the present
19 invention includes a method comprising blending a first synthetic internal olefin having
20 from 16 to 18 carbon atoms, a second synthetic internal olefin having from 15 to 18
21 carbon atoms and a third synthetic internal olefin having from 15 to 16 carbon atoms to
22 form said biodegradable wellbore fluid. In either instance, the inventive method may
23 include blending an alpha olefin having 16 carbon atoms.

24 The present invention includes as an illustrative embodiment a method of drilling
25 a subterranean well. Such an illustrative embodiment includes attaching a cutting bit to a
26 length of drill pipe, rotating said cutting bit, removing cuttings from around said bit with
27 a drilling fluid. The illustrative method utilizes a wellbore fluid as is substantially
28 disclosed herein. In a preferred embodiment, the wellbore fluid includes a first synthetic
29 internal olefin having from 16 to 18 carbon atoms, a second synthetic internal olefin
30 having from 15 to 18 carbon atoms and a third synthetic internal olefin having from 15 to
31 16 carbon atoms.

1

2 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

3 The present invention is generally directed to the continuous phase of a non-
4 aqueous drilling fluid that uses a synthetic material as the continuous phase.

5 The present invention is generally directed to a synthetic material well bore fluid
6 that has a balance of properties including toxicity and biodegradability as well as meeting
7 PAH limitations. The synthetic material based well bore fluid is useful in the formulation
8 of drilling, completing and working over of subterranean wells, preferably oil and gas
9 wells. The fluids of the present invention may also be used as packing fluids, fracturing
10 fluids and other similar well bore uses in which the properties of biodegradability and
11 low toxicity as well as lack of priority pollutants are desired. The fluids of the present
12 invention may also be used to formulate Non-Aqueous Drilling Fluids. Uses of the well
13 bore fluids and non-aqueous drilling fluid should be known to one of skill in the art as is
14 noted in the book COMPOSITION AND PROPERTIES OF DRILLING AND
15 COMPLETION FLUIDS, 5th Edition, H.C.H. Darley and George R. Gray, Gulf
16 Publishing Company, 1988, the contents of which are hereby incorporated herein by
17 reference.

18 An oleaginous fluid is a liquid and more preferably is a synthetic material and
19 more preferably the oleaginous fluid is selected from the group including synthetic
20 internal olefin synthetic alpha olefins and mixtures thereof. The concentration of the
21 oleaginous fluid should be sufficient so that an invert emulsion forms and may be less
22 than about 99% by volume of the non-aqueous drilling fluid emulsion. In one
23 embodiment the amount of oleaginous fluid is from about 30% to about 95% by volume
24 and more preferably about 40% to about 90% by volume of the non-aqueous drilling
25 fluid. The oleaginous fluid in one embodiment includes a mixture of synthetic internal
26 olefins and in another alternative illustrative embodiment the mixture includes alpha
27 olefins in addition to the mixture of synthetic internal olefins. As is illustrated below,
28 such a combination of synthetic internal olefins and optionally alpha olefin results in a
29 drilling fluid having a desirable balance of toxicity and biodegradability. Specifically, in
30 one illustrative core blend embodiment a mixture of a synthetic C₁₆- C₁₈ internal olefin; a
31 synthetic C₁₅- C₁₈ internal olefin; a synthetic C₁₅ - C₁₆ internal olefin has been found to

1 consistently meet the environmental standards for use in the Gulf of Mexico. This
2 consistency of passing the toxicity and biodegradation tests provides a higher level of
3 compliance assurance in contrast to the performance of the individual products which
4 suffer greater variability due to testing artifacts and manufacturing inconsistencies. In
5 another illustrative core blend embodiment, a mixture of a synthetic C₁₆- C₁₈ internal
6 olefin; a synthetic C₁₅- C₁₈ internal olefin; a synthetic C₁₅- C₁₆ internal olefin and a C₁₆
7 alpha olefin has been found to consistently meet the environmental standards for use in
8 the Gulf of Mexico and Effluent Limitation Guidelines. This results in an oleaginous
9 fluid having a balance of toxicity and biodegradability properties as well as meeting the
10 PAH limitations required by the Effluent Limitation Guidelines and the general permits
11 including GMG290000. Specifically, in the second illustrative core blend embodiment a
12 mixture of a synthetic C₁₆- C₁₈ internal olefin; a synthetic C₁₅- C₁₈ internal olefin; a
13 synthetic C₁₅ - C₁₆ internal olefin and a C₁₆ alpha olefin has been found to consistently
14 meet the environmental standards for use in the Gulf of Mexico. This consistency of
15 passing the toxicity and biodegradation tests provides a higher level of compliance
16 assurance in contrast to the performance of the individual products which suffer greater
17 variability due to testing artifacts and manufacturing inconsistencies

18 The present invention also discloses a method of formulating a drilling fluid by
19 first determining the toxicity and biodegradability of the components, and balancing the
20 toxicity and biodegradability of the individual components, for example internal olefins
21 (IO) and/or alpha-olefins (AOs), and then blending them to achieve the desired result. In
22 pursuing the methods of the present invention as applied to aliphatic hydrocarbons, it has
23 been discovered that generally as the molecular weight of the hydrocarbon increases, the
24 hydrocarbon becomes less toxic but also become less biodegradable. The opposite is also
25 true, the lower molecular weight, the hydrocarbon becomes more toxic, but also more
26 biodegradable. Thus we have discovered that it is necessary to balance the blend of
27 hydrocarbons, principally internal olefins and alpha-olefins, to achieve a high molecular
28 weight fluid with good biodegradability and low toxicity. The balance of
29 biodegradability and toxicity occurs in a context of also meeting the PAH requirements
30 of the base stock limitations.

1 In an illustrative embodiment of the present invention, three different internal
 2 olefins (IO's) were tested and utilized: C₁₆-C₁₈ internal olefin (the first internal olefin,
 3 also referred to as the C₁₆₋₁₈ IO), C₁₅-C₁₈ internal olefin (the second internal olefin), and
 4 C₁₅-C₁₆ internal olefin (the third internal olefin). Additionally, a C₁₆ alpha-olefin (AO)
 5 was tested and optionally was added to the mixture of internal olefins. As noted above,
 6 we have discovered that biodegradability generally increases in the following order: C₁₆-
 7 C₁₈ internal olefin; C₁₅-C₁₈ internal olefin; C₁₅-C₁₆ internal olefin; and C₁₆ alpha-olefin
 8 having the highest biodegradability. In contrast, testing of the toxicity generally has the
 9 opposite order with C₁₆-C₁₈ internal olefin having the lowest toxicity; C₁₅-C₁₈ internal
 10 olefin; C₁₆ alpha-olefin and C₁₅-C₁₆ internal olefin having the highest toxicity.

11 As described above, none of the fluids by itself possesses the balance of high
 12 biodegradability and low toxicity achievable by the fluids of the present invention.
 13 However, we have found that a blend of the three internal olefins and optionally the
 14 alpha-olefin produce fluids that balance biodegradability and low toxicity.

15 The following Table 1 shows the typical compositions of the synthetic
 16 hydrocarbons utilized in a preferred illustrative embodiment:

17 TABLE 1

	C ₁₆ -C ₁₈ IO	C ₁₅ -C ₁₈ IO	C ₁₅ -C ₁₆ IO	C ₁₆ AO
C ₁₄ Isomers	0.6	2.7	3.6	1.1
C ₁₅ Isomers	1.0	23.2	48.1	0.5
C ₁₆ Isomers	55.1	25.4	43.3	94.6
C ₁₇ Isomers	2.1	24.0	4.9	0.3
C ₁₈ Isomers	33.0	19.7	0.0	3.4
C ₁₉ Isomers	1.6	5.0	0.0	0.0
C ₂₀ Isomers	6.6	0.0	0.0	0.1

18 All values are in % (w/w).

19 As the term is used in this disclosure a C₁₆₋₁₈ IO is defined as having a C₁₆ isomer
 20 content of greater than 50% w/w and a C₁₈ isomer content greater than 30% w/w. As the
 21 term is used in this disclosure a C₁₅₋₁₈ IO is defined as having a C₁₅ isomer content of
 22 greater than 20% w/w; a C₁₆ isomer content greater than 20%; a C₁₇ isomer content
 23 greater than 20%; and a C₁₈ isomer content greater than 15% w/w. As the term is used in
 24 this disclosure a C₁₅₋₁₆ IO is defined as having a C₁₅ isomer content of greater than 40%

1 w/w and a C₁₆ isomer content greater than 40% w/w. As the term is used in this
 2 disclosure a C₁₆ alpha olefin is defined as having a C₁₆ isomer content of greater than
 3 90% w/w. As indicated in the table above the fluid may contain a mixture of isomers so
 4 long as the content of the other isomers does not exceed those of the isomers that define
 5 the fluid.

6 In the following Table 2, the following mixtures of formulated base fluids have
 7 been included as being illustrative of the base fluids of the present invention:

8 Sample E - 30% internal olefin #1 (C₁₆₋₁₈ IO); 40% internal olefin #2 (C₁₅₋₁₈ IO),,
 9 30% internal olefin #3 (C₁₅₋₁₆ IO),

10 Sample F - 50% internal olefin #1 (C₁₆₋₁₈ IO) and 50% E

11 Sample G - 60% internal olefin #1 (C₁₆₋₁₈ IO) and 40% E

12 Sample H - 40% internal olefin #1 (C₁₆₋₁₈ IO) and 60% E

13 TABLE 2

	E	F	G	H
C ₁₄ Isomers	2.6	1.7	1.5	1.9
C ₁₅ Isomers	23.8	12.4	10.0	14.6
C ₁₆ Isomers	52.1	53.6	54.2	52.9
C ₁₇ Isomers	11.2	7.1	6.2	7.9
C ₁₈ Isomers	8.8	20.4	22.8	18.6
C ₁₉ Isomers	1.6	1.4	1.3	1.4
C ₂₀ Isomers	0.0	3.4	4.0	2.7

14 All values are in % (w/w).

15

16 As the term is utilized in this disclosure, a three-component blend of
 17 hydrocarbons that are illustrative of the present invention comprises about 45 % wt/wt to
 18 about 55 % wt/wt of a C₁₆-C₁₈ internal olefin (internal olefin #1, C₁₆₋₁₈ IO), about 20 %
 19 wt/wt to about 30 % wt/wt of a C₁₅-C₁₈ internal olefin (internal olefin #2, C₁₅₋₁₈ IO), and
 20 about 20 % wt/wt to about 30 % wt/wt of a C₁₅-C₁₆ internal olefin (internal olefin #3,
 21 C₁₅₋₁₆ IO). A preferred blend comprises about 47 % wt/wt to about 53 % wt/wt internal
 22 olefin #1 (C₁₆₋₁₈ IO), about 22 % wt/wt to about 28 % wt/wt internal olefin #2 (C₁₅₋₁₈
 23 IO), and about 22 % wt/wt to about 28 % wt/wt internal olefin #3 (C₁₅₋₁₆ IO). A more

1 preferred blend comprises about 50 % wt/wt internal olefin #1 (C₁₆₋₁₈ IO), about 25 %
2 wt/wt internal olefin #2 (C₁₅₋₁₈ IO), and about 25 % wt/wt internal olefin #3 (C₁₅₋₁₆ IO).

3 As the term is utilized in this disclosure, a four-component blend of hydrocarbons
4 that is illustrative of the present invention comprises about 45 to about 55% internal
5 olefin #1 (C₁₆₋₁₈ IO), about 15 to about 25% internal olefin #2 (C₁₅₋₁₈ IO), about 10 to
6 about 20% internal olefin #3 (C₁₅₋₁₆ IO), and about 10 to about 20% C₁₆ alpha-olefin (C₁₆
7 AO). A preferred blend comprises about 47 to about 53% internal olefin #1 (C₁₆₋₁₈ IO),
8 about 17 to about 23% internal olefin #2 (C₁₅₋₁₈ IO), about 12 to about 18% internal
9 olefin #3 (C₁₅₋₁₆ IO), and about 12 to about 18% C₁₆ alpha-olefin (C₁₆ AO). A more
10 preferred blend comprises about 50 % internal olefin #1 (C₁₆₋₁₈ IO), about 20% internal
11 olefin #2 (C₁₅₋₁₈ IO), about 15% internal olefin #3 (C₁₅₋₁₆ IO), and about 15% C₁₆ alpha-
12 olefin (C₁₆ AO).

13 The drilling fluid of the present invention may optionally contain a non-
14 oleaginous phase. The components of the non-oleaginous phase include, but not limited
15 to, fresh water, seawater, a brine containing organic or inorganic dissolved salts, a liquid
16 containing water-miscible organic compounds, and combinations thereof. The non-
17 oleaginous phase comprises from about 1 to about 70 by volume of the drilling fluid.

18 Various emulsifiers may be added to the drilling fluids of the present invention.
19 The emulsifiers are chemical compounds that have both oleophilic and hydrophilic parts.
20 The emulsifiers that have demonstrated utility in the emulsions of this invention are fatty
21 acids, soaps of fatty acids, amidoamines, polyamides, polyamines, oleate esters, such as
22 sorbitan monoleate, sorbitan dioleate, imidazoline derivatives or alcohol derivatives and
23 combinations or derivatives of the above. Blends of these materials as well as other
24 emulsifiers can be used for this application.

25 A rheology control agent, such as those disclosed in co-pending application
26 entitled: "OIL BASED DRILLING FLUID AND INVERT EMULSION HAVING A FLAT
27 RHEOLOGY" may be utilized to flatten the rheological characteristics of the drilling fluid
28 over a wide temperature range (i.e. from 40° F to 150° F). In one illustrative
29 embodiment, the rheology modifier is a poly-carboxylic acid of a fatty acid. More
30 preferably the poly-carboxylic acid is trimeric and therefore at least three carboxyl groups
31 in the molecule, and more preferably the trimeric poly-carboxylic acid is derived from

1 tall oil or other similar unsaturated long chain carboxylic acids (i.e. fatty acids). A
2 particularly preferred embodiment is commercially available from M-I, of Houston TX as
3 EMI-755. In another illustrative embodiment of the present invention, the rheology
4 modifier is a proprietary polyamide based rheology modifier based on a mixture of
5 amides and amines commercially available from M-I of Houston TX as EMI-756. The
6 concentration of the rheology modifier should be sufficient to achieve the results of the
7 present invention. In one illustrative embodiment in which the rheology modifier is a
8 trimeric poly-carboxylic acid of tall oil, the concentration may range from 0.1 to 5
9 pounds per barrel of drilling fluid and more preferably is from about 0.5 to 2 pounds per
10 barrel of fluid.

11 The method used in preparing the drilling fluids of the present invention is not
12 critical. Conventional methods can be used to prepare the drilling fluids of the present
13 invention in a manner analogous to those normally used, to prepare conventional oil-
14 based drilling fluids. In one representative procedure, a desired quantity of oleaginous
15 fluid such as a base stock that meets environmental regulatory requirement and a suitable
16 amount of the primary emulsifier are mixed together followed by the rheology modifying
17 agent and the remaining components are added with continuous mixing. non-aqueous
18 drilling fluid based on this fluid may be formed by vigorously agitating, mixing or
19 shearing the oleaginous fluid with a non-oleaginous fluid.

20 The fluids of the present invention may further contain additional components
21 depending upon the end use of the non-aqueous drilling fluids so long as they do not
22 adversely impact the toxicity and biodegradability of the fluids described herein. For
23 example, alkali reserve, wetting agents, organophillic clays, viscosifiers, weighting
24 agents, bridging agents and fluid loss control agents may be added to the fluid
25 compositions of this invention for additional functional properties. The addition of such
26 agents should be well known to one of skill in the art of formulating drilling fluids and
27 muds.

28 Wetting agents that may be suitable for use in this invention include, crude tall
29 oil, oxidized crude tall oil, organic phosphate esters, modified imidazolines and
30 amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or
31 derivatives of these. Versawet® and Versawet®NS are examples of commercially

1 available wetting agents manufactured and distributed by M-I L.L.C. that may be used
2 in this invention. Silwet L-77, L-7001, L7605 and L-7622 are examples of
3 commercially available surfactants and wetting agents manufactured and distributed by
4 Union Carbide Chemical Company Inc.

5 Organophilic clays, normally amine treated clays, may be useful as viscosifiers
6 in the fluid compositions of the present invention. The amount of organophilic clay
7 used in the composition should be minimized to avoid an adverse effect upon the
8 rheological properties of the present inventive drilling fluids. However, normally about
9 0.1% to 10% by weight range are sufficient for most applications. VG-69 and VG-
10 PLUS are organo-clay materials distributed by M-I L.L.C., and Versa-HRP is a
11 polyamide resin material manufactured and distributed by M-I L.L.C., that may be
12 used in this invention.

13 Weighting agents or density materials suitable for use in this invention include
14 galena, hematite, magnetite, iron oxides, ilmenite, barite, siderite, celestite, dolomite,
15 calcite, and the like. The quantity of such material added, if any, depends upon the
16 desired density of the final composition. Typically, weight material is added to result
17 in a drilling fluid density of up to about 24 pounds per gallon. The weight material is
18 preferably added up to 21 pounds per gallon and most preferably up to 19.5 pounds per
19 gallon.

20 Fluid loss control agents typically act by coating the walls of the borehole as the
21 well is being drilled. Suitable fluid loss control agents which may find utility in this
22 invention include modified lignites, asphaltic compounds, gilsonite, organophilic
23 humates prepared by reacting humic acid with amides or polyalkylene polyamines, and
24 other non-toxic fluid loss additives that do not cause the drilling fluid to fail the RPE
25 test identified in the guidelines and the permit. Typically, fluid loss control agents are
26 added in amounts less than about 10% and preferably less than about 5% by weight of
27 the fluid.

28 The following examples are included to demonstrate preferred embodiments of
29 the invention. It should be appreciated by those of skill in the art that the techniques and
30 compositions disclosed in the examples which follow represent techniques discovered by

1 the inventors to function well in the practice of the invention, and thus can be considered
 2 to constitute preferred modes for its practice. However, those of skill in the art should, in
 3 light of the present disclosure, appreciate that many changes can be made in the specific
 4 embodiments which are disclosed and still obtain a like or similar result without
 5 departing from the scope of the invention.

6 General Information Relevant to the Examples

7 These tests were conducted in accordance with the procedures in API Bulletin RP
 8 13B-2, 1990. The following abbreviations are sometimes used in describing the results
 9 of experimentation.

10 “PV” is plastic viscosity which is one variable used in the calculation of viscosity
 11 characteristics of a drilling fluid, measured in centipoise (cp) units.

12 “YP” is yield point which is another variable used in the calculation of viscosity
 13 characteristics of drilling fluids, measured in pounds per 100 square feet (lb/100 ft²).

14 “AV” is apparent viscosity which is another variable used in the calculation of
 15 viscosity characteristic of drilling fluid, measured in centipoise (cp) units.

16 “GELS” is a measure of the suspending characteristics, or the thixotropic
 17 properties of a drilling fluid, measured in pounds per 100 square feet (lb/100 ft²).

18 “API F.L.” is the term used for API filtrate loss in milliliters (ml).

19 “HTHP” is the term used for high temperature high pressure fluid loss, measured
 20 in milliliters (ml) according to API bulletin RP 13 B-2, 1990.

21 “Mwt.” is the mud weight in pounds per gallon.

22 The following products are utilized in the following illustrative examples. These
 23 products are commercially available and to the extent know are described.

24 “LAMGREEN P1” is a fatty acid ester based primary surfactant available from
 25 Lamberti Chemical of Milano, Italy

26 “LAMGREEN S1” is a supplemental emulsion with an fatty acid ester base
 27 available from Lamberti Chemical of Milano, Italy

28 “MI BAR” is crushed, sieved and sized barite weighting agent available from M-
 29 I, Inc., Houston, Texas.

30 “VG+” is an organophillic clay viscosity agent available from M-I, Inc., Houston,
 31 Texas.

1 “Benton 990” is an organophillic clay viscosity agent available from M-I, Inc.,
2 Houston, Texas.

3 “VG Supreme” is an organophillic clay viscosity agent available from M-I, Inc.,
4 Houston, Texas.

5 “EMI-715” is an organophillic clay rheology agent available from M-I, Inc.,
6 Houston, Texas.

7 “VERSA HRP” is a polyamide viscosifier available from M-I, Inc., Houston,
8 Texas.

9 “VERSA EMUL-2” is an amidoamine emulsifier available from M-I, Inc.,
10 Houston, Texas.

11 “EMI-526” is a resin based fluid loss control agent available from M-I, Inc.,
12 Houston, Texas.

13 “EMI-595” is an amidoamine emulsifier available from M-I, Inc., Houston,
14 Texas.

15 “EMI-157” is an oleic acid based wetting agent and can be used as a secondary
16 emulsifier available from M-I, Inc., Houston, Texas.

17 “EMI-755” is a trimer acid based rheology modifier available from M-I, Inc.,
18 Houston, Texas.

19 “EcoTrol” is a fluid loss control agent and is available from M-I, Inc., Houston,
20 Texas.

21 The following examples illustrate drilling fluid formulations and their suitability
22 for drilling subterranean wells.

23

24 Example 1: Three-Component Blend:

25 In this example a three component base drilling fluid was utilized in the
26 formulation of an invert emulsion drilling fluid (Mud A). Simulated drilling solids
27 (OCMA clay) were added to invert emulsion to achieve Mud B. The following table
28 provides representative formulation information for each test fluid.

29

<i>Mud Formulation</i>	A	B
IO C ₁₆₋₁₈ , ml	98	98

IO C ₁₅₋₁₈ , ml	49	49
IO C ₁₅₋₁₆ , ml	49	49
VG+, ppb	1.0	1.0
Lime, ppb	3.0	3.0
EMI-595, ppb	7	7
EMI-157, ppb	3	3
EMI-755, ppb	2	2
25% CaCl ₂ brine, ml	70.8	70.8
Barite, ppb	290	290
EcoTrol, ppb	0.5	0.5
OCMA, ppb	-	35

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The rheological properties of both the base invert emulsion (mud A) and the base invert emulsion including simulated drilling cuttings were determined both prior to and after hot rolling for about 16 hours at about 150°F.

Barite sag control was tested using a sag flow loop tester. About 2.8 gallons of the test mud is circulated in the flow loop consisting of a plastic test tube (2" ID x 6' long), a circulating pump, and a densitometer. The plastic tube can be adjusted at angles varying from vertical (0-degree) to horizontal (90-degree). Inside the plastic tube, a steel rod is used to simulate drill string and can be rotated at speeds varying from 0 to 225 rpm. For barite sag evaluation, the test normally is conducted at 60-degree inclination with varying pump rates (from 25 to 185 fpm annular velocity) and pipe rotations (from 0 to 225 rpm). Changes of mud weight due to sagging/settling of barite or other weighting agent in the test tube are determined by the densitometer under circulating conditions. After the sag test, the mud weight data were corrected to a constant temperature of 120°F for comparison.

The following table provides representative data for the base invert emulsion (mud A).

1 **Mud A**

<u>Mud Properties</u>							
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		
	Before Hot Rolling				After Hot Rolling @150°F		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	73	53	40		140	63	46
300 rpm	42	30	23		84	35	29
200 rpm	33	23	17		61	28	22
100 rpm	21	15	11		36	19	16
6 rpm	6	5	5		9	8	9
3 rpm	5	4	4		7	7	8
PV, cps	31	23	17		56	28	17
YP, lbs/100 ft ²	11	7	6		28	7	12
10 Second Gel	7	6	6		14	13	12
10 Minute Gel	9	8	8		20	23	18
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	255				436		
<u>SAG TEST @150°F</u>							
VST, ppg	-				2.8		

2

3 The following table provides representative data for the base invert emulsion with
4 the addition of 35 pounds per barrel (ppb) of OCMA clay a simulated drilling solids
5 material (mud B).

6

7 **Mud B (Base fluid (Mud A) plus 35 ppb simulated drilling solids)**

<u>Mud Properties</u>							
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		

	Before Hot Rolling				After Hot Rolling @150°F		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	134	104	77		211	99	74
300 rpm	84	69	50		125	61	52
200 rpm	67	55	42		92	48	45
100 rpm	48	41	32		57	34	36
6 rpm	23	21	17		18	20	27
3 rpm	22	19	17		16	20	25
PV, cps	50	35	27		86	38	22
YP, lbs/100 ft ²	34	34	23		39	23	30
10 Second Gel	23	22	18		23	29	29
10 Minute Gel	32	29	28		49	43	37
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	679				880		
<u>SAG TEST @150°F</u>							
VST, ppg	2.8				0.13		

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2 Upon review of the above data, one of skill in the art should understand and
3 appreciate that fluids formulated in accordance with the present invention are suitable for
4 use as a non-aqueous drilling fluid in the drilling of subterranean wells.

5

6 Example 2: Four Component Blend

7 In this example a four component base drilling fluid was utilized in the
8 formulation of a non-aqueous drilling fluid (Mud C). Simulated drilling solids (OCMA
9 clay) were added to non-aqueous drilling fluid to achieve Mud D. The following table
10 provides representative formulation information for each test fluid.

11

<u>Fluid Formulation</u>	<i>C</i>	<i>D</i>
IO C ₁₆₋₁₈ , ppb	77.12	77.12

IO C ₁₅₋₁₈ , ppb	30.85	30.85
IO C ₁₅₋₁₆ , ppb	23.13	23.13
AO C ₁₆ , ppb	23.13	23.13
VG+, ppb	2.0	2.0
Lime, ppb	3.0	3.0
Lamgreen P1, ppb	7	7
Lamgreen S1, ppb	2	2
25% CaCl ₂ brine, ppb	87.1	87.1
EMI-526	1	1
MI BAR, ppb	289.15	289.15
OCMA, ppb	-	35

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The rheological properties of both the base invert emulsion (mud C) and the base non-aqueous drilling fluid including simulated drilling cuttings (Mud D) were determined after hot rolling for about 16 hours at about 150°F. The following table provides representative data for both formulations.

<i>Mud Properties</i>	C				D		
Heat aging Temp. °F	150				150		
Heat Aging Time Hrs.	16				16		
Static/Rolling	Rolling				Rolling		
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	124	54	39		160	76	55
300 rpm	77	35	26		94	45	35
200 rpm	58	24	16		71	32	23
100 rpm	39	16	11		46	21	15
6 rpm	13	6	5		13	7	5
3 rpm	11	5	4		10	5	4
PV, cps	47	19	13		66	31	20
YP, lbs/100 ft ²	30	16	13		28	14	15
10 Second Gel	13	6	5		14	7	6
10 Minute Gel	14	7	6		15	8	8
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	684				796		
<u>SAG TEST @150°F</u>	12.917				13.334		
Initial Mwt. Ppg							
Bottom Mwt, ppg	16.000				15.459		
Top Mwt, ppg	11.584				11.834		
VST, ppg	3.083				2.212		

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Upon review of the above data one of skill in the art should understand and appreciate that the above fluid formulations are suitable for drilling subterranean wells. Further it should be noted that no barite settling was observed after cooling down to room temperature.

1 Example 3: Rheology Modifiers

2 In this example a four component base drilling fluid was utilized in the
 3 formulation of a non-aqueous drilling fluid (Mud C) but also including a rheology agent.
 4 Simulated drilling solids (OCMA clay) were added to the non-aqueous drilling fluid .
 5 The following table provides representative formulation information for each test fluid.

6

<u><i>Fluid Formulation</i></u>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
	<i>Base</i>	<i>Mud C & EMI-715</i>	<i>Mud C & Emul-2</i>	<i>Mud C & Versa HRP</i>
IO C ₁₆₋₁₈ , ppb	77.12	77.12	77.12	77.12
IO C ₁₅₋₁₈ , ppb	30.85	30.85	30.85	30.85
IO C ₁₅₋₁₆ , ppb	23.13	23.13	23.13	23.13
AO C ₁₆ , ppb	23.13	23.13	23.13	23.13
VG+, ppb	2.0	2.0	2.0	2.0
Lime, ppb	3.0	3.0	3.0	3.0
Lamgreen P1, ppb	7	7	7	7
Lamgreen S1, ppb	2	2	2	2
25% CaCl ₂ brine, ppb	87.1	87.1	87.1	87.1
EMI-526	1	1	1	1
MI BAR, ppb	289.15	289.15	289.15	289.15
Rheology Agent, ppb	-	0.5	1.5	1.0

7
 8 The rheological properties of both the non-aqueous drilling fluids (Muds E, F and
 9 G) and the base non-aqueous drilling fluid including simulated drilling cuttings (Muds
 10 E', F' and G') were determined after hot rolling for about 16 hours at about 150°F. The
 11 following tables provide representative data.

12

<i>Mud Properties</i>	Mud E				Mud E' (25 ppb OCMA clay)		
Heat aging Temp. °F	150				150		
Heat Aging Time Hrs.	16				16		
Static/Rolling	Rolling				<i>Rolling</i>		
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	155	74	55		170	84	64
300 rpm	90	46	36		98	53	44
200 rpm	66	35	26		73	42	34
100 rpm	42	33	19		47	27	25
6 rpm	13	11	10		16	12	12
3 rpm	11	10	9		13	11	11
PV, cps	65	28	19		72	31	20
YP, lbs/100 ft ²	25	18	17		26	22	24
10 Second Gel	16	13	13		18	17	14
10 Minute Gel	21	19	20		28	25	22
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	765				810		
<u>SAG TEST @150°F</u>	13.292				13.375		
Initial Mwt. Ppg							
Bottom Mwt, ppg	15.209				14.584		
Top Mwt, ppg	11.584				-		
VST, ppg	1.917				1.208		

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<i>Mud Properties</i>	Mud F				Mud F' (25 ppb OCMA clay)		
Heat aging Temp. °F	150				150		
Heat Aging Time Hrs.	16				16		
Static/Rolling	Rolling				<i>Rolling</i>		
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	149	72	54		182	89	69
300 rpm	92	47	38		107	57	48
200 rpm	71	34	28		80	46	37
100 rpm	47	24	21		52	32	27
6 rpm	16	12	11		18	16	16
3 rpm	14	11	10		16	14	14
PV, cps	57	25	16		75	32	21
YP, lbs/100 ft ²	35	22	22		32	25	27
10 Second Gel	19	15	11		22	21	18
10 Minute Gel	28	21	16		38	29	24
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	694				804		
<u>SAG TEST @150°F</u>	12.91				13.31		
Initial Mwt. Ppg							
Bottom Mwt, ppg	14.33				14.33		
Top Mwt, ppg	12.03				12.42		
VST, ppg	1.42				1.02		

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<i>Mud Properties</i>	Mud G				Mud G' (25 ppb OCMA clay)		
Heat aging Temp. °F	150				150		
Heat Aging Time Hrs.	16				16		
Static/Rolling	Rolling				Rolling		
Mud Weight, ppg	13.0				13.0		
Synthetic/Water Ratio	75/25				75/25		
Rheo Temp, °F	40	100	150		40	100	150
600 rpm	163	77	55		170	91	72
300 rpm	102	50	38		102	51	50
200 rpm	78	37	28		79	46	42
100 rpm	52	25	20		52	32	32
6 rpm	18	13	13		18	17	20
3 rpm	16	11	12		15	16	18
PV, cps	61	27	17		68	40	22
YP, lbs/100 ft ²	41	23	21		34	11	28
10 Second Gel	21	19	15		23	24	21
10 Minute Gel	38	25	17		38	31	30
Total HTHP@250°F, cc							
E.S. @ 150°F, Volts	823				1048		
<u>SAG TEST @150°F</u>	12.81				12.96		
Initial Mwt. Ppg							
Bottom Mwt, ppg	14.75				14.37		
Top Mwt, ppg	11.37				11.33		
VST, ppg	1.94				1.41		

1
2 Upon review of the above data one of skill in the art should understand and
3 appreciate that the above fluid formulations are suitable for drilling subterranean wells.
4 Further it should be noted that in most cases no or very little syneresis or barite settling
5 was observed after cooling down to room temperature.

1 Sediment Toxicity Testing:

2 To determine the toxicity score of the drilling fluid compositions of the present
3 invention, the bioassays were conducted using previously referenced Static 10-Day
4 Sediment Toxicity Test (STT) of the drilling base fluid. The toxicity score tests were
5 conducted in accordance with the procedures in "Standard Guide for Conducting 10-day
6 Static Sediment Toxicity Tests with Marine and Estuarine Amphipods," ASTM E 1367 -
7 92 & Appendix A of GMG290000. Synthetic seawater and natural sediment was used to
8 culture *L. plumuloius* amphipods. The standard reference toxicant was potassium
9 chloride was used without sediment to measure a 96-hour LC₅₀.

10 Six treatment concentrations were prepared with natural sediment, five of which
11 contained the drilling fluid blend, and one negative control. The sediment was first
12 sieved through 1000 and 500 micrometer sieves. The test concentrations were 1300,
13 2900, 6400, 14,300, and 31,700 milligrams of drilling fluid blend per kilogram of dry
14 natural sediment. Eight hundred milliliters of each sample were prepared. Each sample
15 was mixed for ten minutes with a hand-held mixer.

16 For the definitive test, five replicates with 20 *L. Plumulosus* were exposed to the
17 natural sediment spiked with the base stock drilling fluid blend in the 5 samples above
18 and the control. Each replicant contained approximately 150 milliliters of natural
19 sediment and 600 milliliters 20 ppt overlying water. Treatments were kept in a dedicated
20 environmental chamber with 14 hours of light and 10 hours of dark at 20 °C. After 10
21 days, all five replicates at each treatment were terminated and final survival data
22 recorded. At 24- hour intervals, temperature, DO, pH, and salinity were measured in
23 each treatment. The test was also aerated. Initial 0-hour and 10-day dry weights and 0-
24 hour lengths of representative test organisms were measured. The 10-day weight is from
25 surviving concurrent control organisms.

26 A group of test samples using a reference C₁₆₋₁₈ internal olefin Synthetic Base
27 Fluid (SBF) test was initiated concurrently in a separate aliquot of the same batch of
28 natural sediment as above.

29 The following results are based on representative data:

1 Sediment Toxicity

2 Below represents the summary toxicity score data of three component blend and four
 3 component blend.

4

Blend (C ₁₆₋₁₈ IO #1/ C ₁₅₋₁₈ IO #2/ C ₁₅₋₁₆ IO #3)	LC ₅₀ of Reference	LC ₅₀ of Blend	LC ₅₀ for blend + K Factor	Pass/Fail Limit	Test ratio with K factor	Pass/Fail
50/25/25	3157	7213	7844.4	1	0.4	PASS
25/50/25	3157	2975	3606.4	1	0.9	PASS
25/25/50	3157	2573	3204.4	1	1.0	PASS
30/70/0	3080	5747	6363	1	0.5	PASS
70/30/0	6207	9071	10312.4	1	0.6	PASS
60/0/40	3157	4950	5581.4	1	0.6	PASS
40/0/60	3157	2935	3566.4	1	0.9	PASS

5

Blend (C ₁₆₋₁₈ IO #1/ C ₁₅₋₁₈ IO #2/ C ₁₅₋₁₆ IO #3/ C ₁₆ AO)	LC ₅₀ of Reference	LC ₅₀ of Blend	LC ₅₀ for blend + K Factor	Pass/Fail Limit	Test ratio with K factor	Pass/Fail
50/20/15/ 15	3299	3437	4096.8	1	0.8	PASS
50/30/10/ 10	3299	2558	3217.8	1	1.0	PASS
50/15/20/ 15	2139	3688	4115.8	1	0.5	PASS
50/10/30/ 10	3299	2598	3257.8	1	1.0	PASS
60/20/10/ 10	3299	2893	3552.8	1	0.9	PASS
40/20/20/ 20	3299	6053	6712.8	1	0.5	PASS

70/30/0/0	6207	9071	10312.4	1	0.6	PASS
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Upon consideration, one of skill in the art should understand and appreciate that the fluids of the present invention meet the standard desired for sediment toxicity.

Biodegradability Testing:

The test protocol used for biodegradability tests is in Appendix 4 to Subpart A of Part 435 -- Protocol for the Determination of Biodegradation of Synthetic Base Fluids in a Marine Closed Bottle Test System: Summary of Modifications to ISO 11734:1995. Typically, tests were conducted at 29 °C in anaerobic conditions in a closed bottle using marine/estuarine sediment. Monitoring gas production due to microbial degradation of the test fluid assesses base fluid degradation rates. The biodegradation rate ratio is calculated using the following formula:

$$\text{Biodegradation rate ratio} = (\% \text{ degradation of a reference base stock}) / (\% \text{ degradation of test base stock} + 4\%)$$

To pass the test, the biodegradation rate ratio should be ≤ 1.0

The following table contains the representative results of the biodegradation tests of the individual components as well as the blends of the blends in the present invention.

Blend (C ₁₆₋₁₈ IO #1/ C ₁₅₋₁₈ IO #2/ C ₁₅₋₁₆ IO #3)	Reference Material degradation	Test Material degradation	Regulatory Limit	Test Ratio for all data included	Pass / Fail
50/25/25	52.80	53.27	≤ 1.0	0.9	Pass
25/50/25	52.80	59.52	≤ 1.0	0.8	Pass
25/25/50	52.80	59.40	≤ 1.0	0.8	Pass
30/70/0	52.80	61.30	≤ 1.0	0.8	Pass
70/30/0	52.80	52.04	≤ 1.0	0.9	Pass
60/0/40	52.80	55.40	≤ 1.0	0.9	Pass
40/0/60	52.80	61.40	≤ 1.0	0.8	Pass

Blend (C ₁₆₋₁₈ IO #1/	Reference Material	Test Material degradation	Regulatory Limit	Test Ratio for all data	Pass / Fail
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C ₁₅₋₁₈ IO #2/ C ₁₅₋₁₆ IO #3/ C ₁₆ AO)	degradation			included	
50/20/15/15	40.32	58.63	≤1.0	0.6	Pass
50/30/10/10	40.32	58.23	≤1.0	0.6	Pass
50/15/20/15	40.32	56.50	≤1.0	0.7	Pass
50/10/30/10	40.32	52.55	≤1.0	0.7	Pass
60/20/10/10	40.32	54.91	≤1.0	0.7	Pass
40/20/20/20	40.32	54.91	≤1.0	0.7	Pass
70/30/0/0	52.8	52.0	≤1.0	1.0	Pass

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2 Upon consideration, one of skill in the art should understand and appreciate that

3 the fluids of the present invention meet the standard desired for biodegradability.

4 In view of the above disclosure, one of skill in the art should understand and

5 appreciate that one illustrative embodiment of the present invention includes a first

6 synthetic internal olefin having from 16 to 18 carbon atoms (C₁₆₋₁₈ IO), a second synthetic

7 internal olefin having between 15 to 18 carbon atoms (C₁₅₋₁₈ IO), and a third synthetic

8 internal olefin having 15 to 16 carbon atoms (C₁₅₋₁₆ IO). As the term is used in this

9 disclosure a C₁₆₋₁₈ IO is defined as having a C₁₆ isomer content of greater than 50% w/w

10 and a C₁₈ isomer content greater than 30% w/w. As the term is used in this disclosure a

11 C₁₅₋₁₈ IO is defined as having a C₁₅ isomer content of greater than 20% w/w; a C₁₆ isomer

12 content greater than 20%; a C₁₇ isomer content greater than 20%; and a C₁₈ isomer

13 content greater than 15% w/w. As the term is used in this disclosure a C₁₅₋₁₆ IO is

14 defined as having a C₁₅ isomer content of greater than 40% w/w and a C₁₆ isomer content

15 greater than 40% w/w. As the term is used in this disclosure a C₁₆ alpha olefin is defined

16 as having a C₁₆ isomer content of greater than 90% w/w. As indicated above the fluid

17 may contain a mixture of isomers so long as the content of the other isomers does not

18 exceed those of the isomers that define the fluid. The components of the illustrative

19 wellbore fluid are blended such that the desired characteristics of toxicity and

20 biodegradability are balance to achieve compliance with environmental requirements for

21 hydrocarbon based drilling fluids. One such illustrative embodiment achieves this result

22 by utilizing a formulation in which the first internal olefin is present in a range of about

23 40 to about 60 percent by weight of the wellbore fluid and wherein the second internal

24 olefin is present in range of about 15 to about 40 percent by weight of the wellbore fluid

1 and wherein the third olefin is present in range of about 10 to about 30 percent by weight
2 of the wellbore fluid. Optionally, the illustrative fluid can include a C₁₆ alpha olefin. In
3 such instances, the C₁₆ alpha olefin is present in the range of about 10 to about 20 percent
4 by weight of the wellbore fluid. A person of skill in the art should understand and
5 appreciate that the illustrative wellbore fluid may further include a non-oleaginous phase,
6 typically as an internal phase. By doing so a non-aqueous drilling fluid is preferably
7 formed. When included the non-oleaginous phase constitutes from about 1% to about
8 70% by volume of said fluid. Such a non-oleaginous phase may be selected from fresh
9 water, seawater, a brine containing organic or inorganic dissolved salts, a liquid
10 containing water-miscible organic compounds, and combinations thereof. The fluids of
11 the present invention may further contain additional components depending upon the end
12 use of the non-aqueous drilling fluid so long as they do not adversely impact the toxicity
13 and biodegradability of the fluids or other permit considerations described herein. For
14 example, alkali reserve, wetting agents, organophillic clays, viscosifiers, weighting
15 agents, bridging agents and fluid loss control agents may be added to the fluid
16 compositions of this invention for additional functional properties. The addition of such
17 agents should be well known to one of skill in the art of formulating drilling fluids and
18 muds. When included the weighting agent is selected from the group including calcium
19 carbonate, dolomite, siderite, barite, celestite, iron oxides, manganese oxides, ulexite,
20 carnalite, sodium chloride and combinations thereof and similar such weighting agents
21 known in the art.

22 Alternatively, the present invention is considered to be a method of formulating
23 the continuous phase of a hydrocarbon based drilling fluid. Specifically, in one
24 illustrative core blend embodiment a first synthetic internal olefin having from 16 to 18
25 carbon atoms (C₁₆₋₁₈ IO), a second synthetic internal olefin having between 15 to 18
26 carbon atoms (C₁₅₋₁₈ IO), and a third synthetic internal olefin having 15 to 16 carbon
27 atoms (C₁₅₋₁₆ IO) has been found to consistently meet the environmental standards for use
28 in the Gulf of Mexico. This consistency of passing the toxicity and biodegradation tests
29 provides a higher level of compliance assurance in contrast to the performance of the
30 individual products which suffer greater variability due to testing artifacts and
31 manufacturing inconsistencies. In another illustrative core blend embodiment, a first

1 synthetic internal olefin having from 16 to 18 carbon atoms (C_{16-18} IO), a second synthetic
2 internal olefin having between 15 to 18 carbon atoms (C_{15-18} IO), a third synthetic internal
3 olefin having 15 to 16 carbon atoms (C_{15-16} IO) and a C_{16} alpha olefin has been found to
4 consistently meet the environmental standards for use in the Gulf of Mexico and Effluent
5 Limitation Guidelines. This results in an oleaginous fluid having a balance of toxicity
6 and biodegradability properties as well as meeting the PAH limitations required by the
7 Effluent Limitation Guidelines and the general permits including GMG290000.
8 Specifically, in the second illustrative core blend embodiment a mixture of a synthetic
9 C_{16} - C_{18} internal olefin; a synthetic C_{15} - C_{18} internal olefin; a synthetic C_{15} - C_{16} internal
10 olefin and a C_{16} alpha olefin has been found to consistently meet the environmental
11 standards for use in the Gulf of Mexico. This consistency of passing the toxicity and
12 biodegradation tests provides a higher level of compliance assurance in contrast to the
13 performance of the individual products which suffer greater variability due to testing
14 artifacts and manufacturing inconsistencies

15 One of skill in the art should also appreciate and understand that the present
16 invention includes as an illustrative embodiment a method of drilling a subterranean well
17 Such an illustrative embodiment includes attaching a cutting bit to a length of drill pipe,
18 rotating said cutting bit, removing cuttings from around said bit with a drilling fluid. The
19 illustrative method utilizes a wellbore fluid as is substantially disclosed herein. In a
20 preferred embodiment, the wellbore fluid includes a first synthetic internal olefin having
21 from 16 to 18 carbon atoms (C_{16-18} IO), a second synthetic internal olefin having between
22 15 to 18 carbon atoms (C_{15-18} IO), and a third synthetic internal olefin having 15 to 16
23 carbon atoms (C_{15-16} IO). Optionally the wellbore fluid may include an alpha olefin
24 having 16 carbon atoms (C_{16} AO).

25 While the apparatus, compositions and methods of this invention have been
26 described in terms of preferred or illustrative embodiments, it will be apparent to those of
27 skill in the art that variations may be applied to the process described herein without
28 departing from the concept and scope of the invention. All such similar substitutes and
29 modifications apparent to those skilled in the art are deemed to be within the scope and
30 concept of the invention as it is set out in the following claims.

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